

ON THE RAMAN AND INFRA RED SPECTRA OF BENZOYL CHLORIDE IN DIFFERENT STATES

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(Plate 8)

ABSTRACT. The Raman spectra of benzoyl chloride in liquid and solid states and of the solutions of the molecule in chloroform, carbon tetrachloride, methylene chloride, benzene and chlorobenzene as well as the infrared spectra of the compound in the vapour state and of solutions of different concentrations in benzene, carbon tetrachloride and chloroform have been investigated. It has been concluded from the results that the two bands at 1778 cm^{-1} and 1735 cm^{-1} persist in the spectra of the compound in all the states mentioned above, but their relative intensities depend on concentration of the solutions only in low concentration ranges.

From a comparison of the Raman spectra of cinnamyl chloride and phenylacetyl chloride it has been concluded that line 1735 cm^{-1} is produced by the vibration involving $\text{C}=\text{O}$ stretching in the $\text{Cl}-\text{C}=\text{O}$ group in the molecule in which the plane of the $\text{Cl}-\text{C}=\text{O}$ group is rotated about $\text{C}-\text{C}$ bond through 90° from the plane of the phenyl group. The line 1778 cm^{-1} has been attributed to the same vibration in the molecule having a configuration in which the $\text{Cl}-\text{C}=\text{O}$ group and the phenyl group lie in the same plane. The appearance of two such bands in the infra red spectra of solutions of substituted benzoyl chlorides has also been accounted for on this hypothesis. It has been pointed out that the hydrogen atom of chloroform is mainly responsible for increasing the population of the molecules of non-planar configuration mentioned above in the solution.

It has further been concluded that in the solutions of some of the lactones studied by previous workers the configuration of a particular ring containing the $\text{C}=\text{O}$ group is changed by the hydrogen atom of the solvent molecule to a bent configuration which gives the lower $\text{C}=\text{O}$ frequency.

INTRODUCTION

It is well known that the Raman spectrum of benzoyl chloride in the liquid state shows two lines at 1778 cm^{-1} and 1735 cm^{-1} respectively due to the $\text{O}=\text{C}$ stretching vibration and the relative intensities of these two lines change when the liquid is dissolved in different solvents. However, in the case of any particular solution the intensity-ratio remains unaltered when the concentration is changed by 200 times as pointed out by Jones *et al* (1959) who also observed that the ratio of the intensities of the two lines due to the liquid changes from 1.7 to 2.2 when the temperature of the liquid is changed from 23°C to 102°C . They also observed a similar doublet due to $\text{C}=\text{O}$ stretching vibration in a number of lactones of widely different structures and concluded that Fermi-resonance between this vibration and the overtone of a vibration of about half the frequency can not

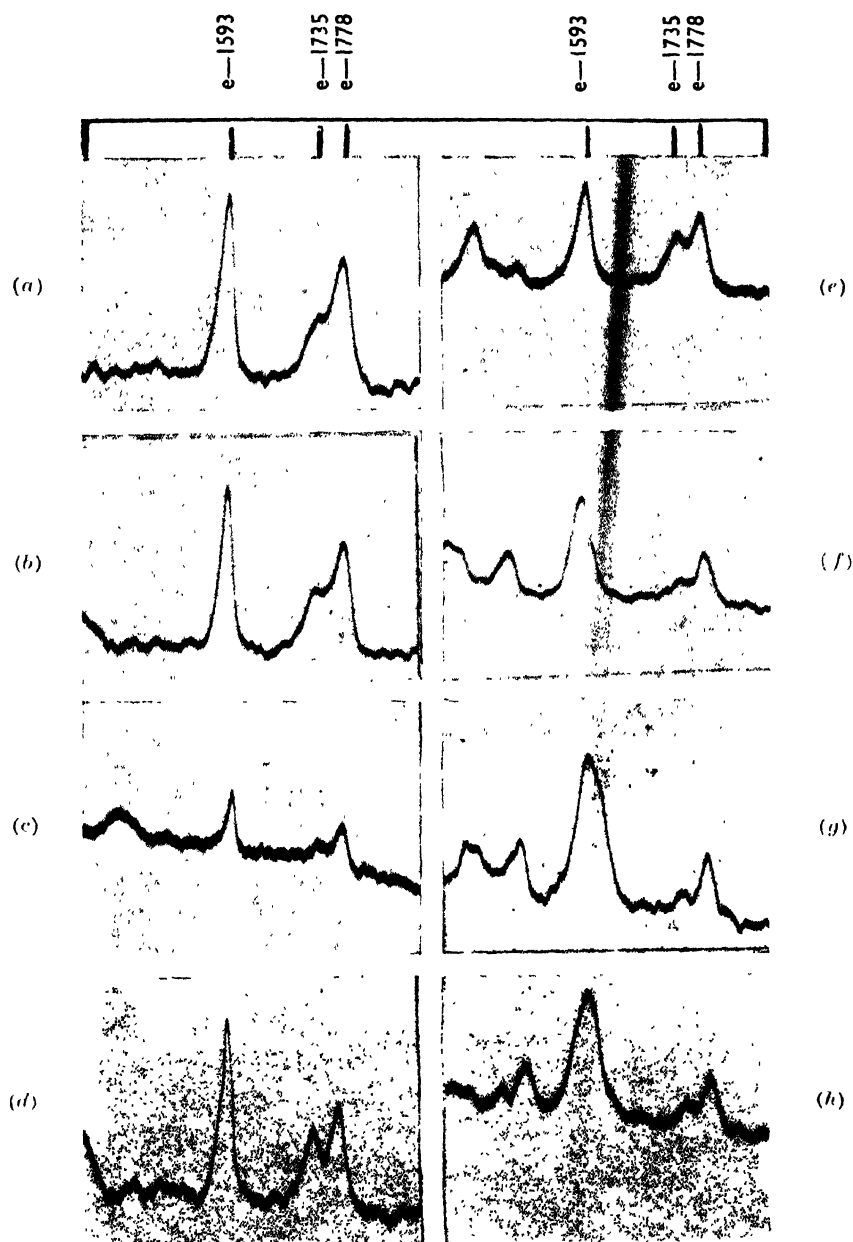
be responsible for the appearance of two Raman lines in the spectra of these molecules having such widely different structures. Forbes and Myron (1961) later made extensive study of the infra red spectra of ortho-, meta- and para- substituted benzoyl chlorides and found two bands due to $C=O$ stretching vibration in each case, the relative intensities of the bands depending on the nature and position of the substituents. They concluded that although in the case of benzoyl chloride Fermi-resonance between the overtone of the vibration of frequency 875 cm^{-1} and the $C=O$ stretching vibration could explain the two bands, in some other cases the overtone was far away from $C=O$ frequency, but as alternative explanations such as intermolecular interactions or the existence of different conformational isomers in equilibrium are more unsatisfactory the most probable explanation was that the doublet occurred because of an intermolecular vibration.

Rao and Venkataraghavan (1962) studied the infrared spectra of a few para-substituted benzoyl chlorides and concluded that in these cases the appearance of the second band near the band due to $C=O$ stretching vibration was connected with the appearance of the band at about 875 cm^{-1} and therefore the second band might be due to Fermi-resonance mentioned above. The results reported by them, however, show that although the overtone should have a value about 1760 cm^{-1} in the cases of four of the six compounds studied by them the frequencies observed by them range from 1735 cm^{-1} to 1744 cm^{-1} and the relative strengths of the two bands are different in the different cases. Hence the explanation based on Fermi-resonance between the two vibrations is not quite satisfactory.

The object of the present investigation was to study the Raman spectra of benzoyl chloride in the solid state at about 90°K and its solutions in different solvents and also the infra red spectrum of the molecule in the vapour state to find out whether the positions and the relative intensities of the two lines 1778 cm^{-1} and 1735 cm^{-1} change with change of state and with change of concentration of the solutions and also to find out the probable causes for the appearance of the second line due to $C=O$ vibration in the spectra of the molecule mentioned above.

EXPERIMENTAL

The infra red spectra of the solutions and of the pure liquid were recorded with a Perkin-Elmer model 21 infrared spectrophotometer provided with NaCl optics. A compensation cell filled with the solvent was used in the reference beam in the case of each of the solutions. The spectrum for the compound in the vapour state was recorded with a one-metre gas cell supplied by Perkin-Elmer. It was found initially that unless special precautions were taken the spectrum of a very thin film of the liquid deposited on the surfaces of the mirrors in the cell was superposed on the spectrum due to the vapour. To avoid this difficulty the cell had been slightly heated and evacuated before the vapour was introduced into it from

Figure 1. Raman spectra of $\text{C}_6\text{H}_5\text{COCl}$ (a) Pure liquid at 95°C (b) " " " 10°C (c) Solid at — 180°C (d) 15% Solution in CHCl_3 (e) 18% Solution in CH_2Cl_2 (f) 15% " " C_6H_6

(g) 5% " " " "

(h) 5% Solution in $\text{C}_6\text{H}_5\text{Cl}$

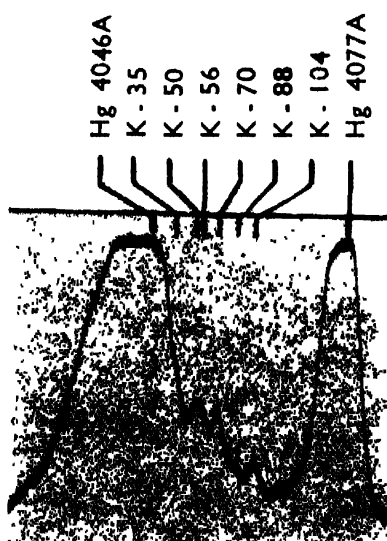


Figure 4. Raman spectrum of C_6H_5COCl at $-180^\circ C$

a bulb containing the liquid at a little lower temperature. The spectrum due to the pure liquid was recorded using a very thin film enclosed between two NaCl plates, a pair of similar plates being placed in the reference beam.

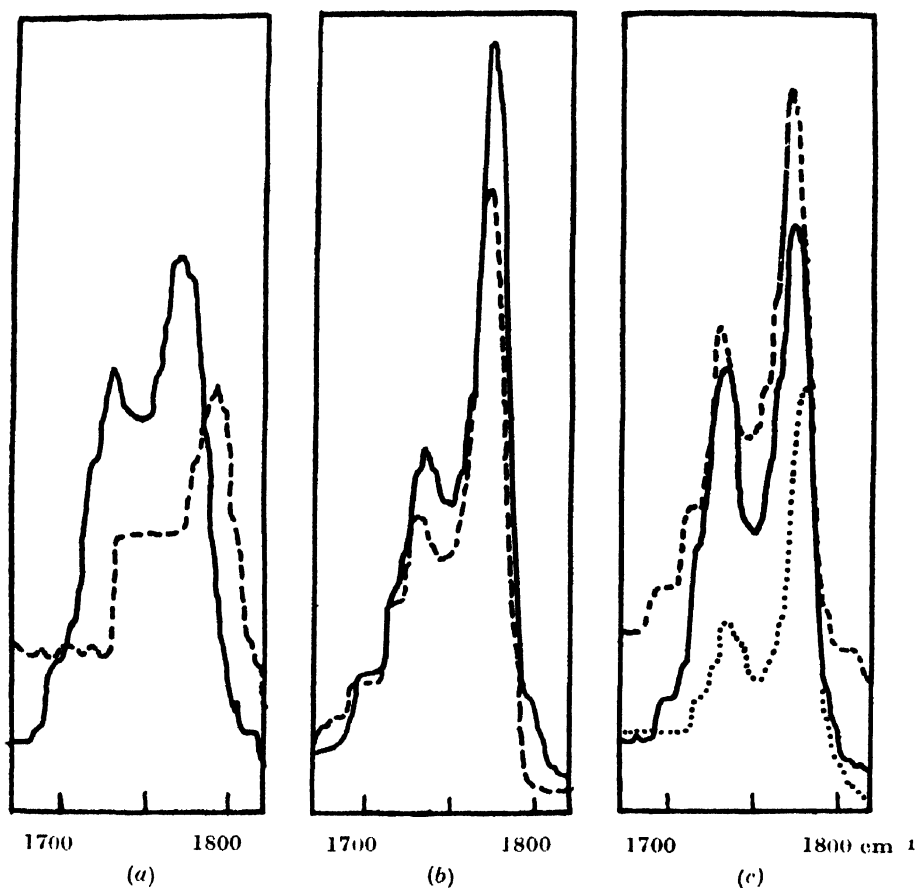
The Raman spectra were photographed using a Fuess glass spectrograph having an inverse dispersion of about 14.5Å/mm near 4358 Å. The Raman spectra of the liquid at 10°C and 95°C were recorded by allowing water at these two temperatures to flow through a jacket surrounding the Raman tube. The Raman spectrum of the substance in the solid state at about -180°C was photographed using liquid oxygen in a Pyrex Dewar vessel as the refrigerant. The liquid supplied by Fischer and Co. and the solvents used for studying the spectra of the solutions were distilled under reduced pressure to get rid of fluorescent impurities. Besides chloroform, methylene chloride and benzene, chlorobenzene was also used as a solvent to find out the nature of influence of the permanent dipole on the Raman spectrum of the benzyl chloride molecule.

An attempt was made to estimate the relative intensities of the lines 1735 cm⁻¹ and 1778 cm⁻¹ in the different Raman spectra. For this purpose intensity marks were taken on a plate from the same packet using a tungsten filament lamp as the source of continuous radiation and different known widths of the slit of the spectrograph. Microphotometric records of these continuous spectra and of the Raman spectra were taken with a Kipp and Zonen self-recording microphotometer. The positions of infinite density were also marked on these records. A blackening-log-intensity curve for the region near 4716 Å was drawn with the help of these records and the relative intensities of the two lines 1735 cm⁻¹ and 1778 cm⁻¹ were determined from the densities of these lines after making correction for the background.

RESULTS AND DISCUSSION

Microphotometric records of the Raman spectra of pure benzoyl chloride at 95°C, 10°C and -180°C and of solutions in chloroform, methylene chloride, benzene and chlorobenzene are reproduced in figures 1(a)-1(h), respectively. Tracings of the records of the infra red spectra of the molecule in the liquid and vapour states are given in figure 2(a). Figure 2(b) shows the spectra due to 3% and 1% solutions in benzene and figure 2(c) shows those of the solutions in chloroform and carbon tetrachloride. The dotted curve in figure 2(c) is due to a 0.2% solution in carbon tetrachloride. The relative intensities of the two Raman lines 1735 cm⁻¹ and 1778 cm⁻¹ determined from the records shown in figures 1(a)-1(h) (Plate 8A) are given in table 1.

It can be seen from table 1 that the ratio of intensities of the two lines 1735 cm⁻¹ and 1778 cm⁻¹ diminishes not only when the temperature of the liquid is raised from 10°C to 95°C but also when the frozen liquid is cooled to -180°C. The ratio diminishes from 1 : 1.74 to 1 : 2.2 when the liquid is dissolved in benzene

Fig. 2. Infrared spectra of $\text{C}_6\text{H}_5\text{COCl}$

- (a)—Pure liquid, Vapour
 (b)—4% Soln. in C_6H_6 , Cell 0.1 mm, 3% Soln in C_6H_6 , (.025 mm)
 (c)—2% Soln. in CHCl_3 , 2% Soln. in CCl_4 , 0.2% Soln in CCl_4

Table 1

Intensity-ratio of two $\text{C}=\text{O}$ frequencies of benzoyl chloride

Experimental condition	$I_{1735} : I_{1778}$
Liquid at 95°C	1 : 2.40
Liquid at 10°C	1 : 1.74
Solid at -180°C	1 : 2.3
15% Solution in CHCl_3	1 : 1.40
18% Solution in CH_2Cl_2	1 : 1.50
15% Solution in C_6H_6	1 : 2.20
5% Solution in C_6H_6	1 : 3.0
5% Solution in $\text{C}_6\text{H}_5\text{Cl}$	1 : 2.30

to make a 15% solution and it diminishes still further to 1 : 3.0 when the concentration is reduced to 5%. On the other hand, the ratio increases to 1 : 1.4 and 1 : 1.50 respectively in the cases of 15% solution in chloroform and 18% solution in methylene chloride. In the case of 5% solution in chlorobenzene, however, the ratio is 1 : 2.30 which is smaller than that for the pure liquid. Thus in the concentration range 15% to 5% of the solution in benzene the ratio depends slightly on concentration and also the C-Cl group of the chlorobenzene molecule has an influence different from that of the C-H group of the chloroform molecule on the ratio of the intensities of the two lines.

Records of the infrared spectra reproduced in figure 2(a) show that the bands 1735 cm^{-1} and 1778 cm^{-1} shift to about 1752 cm^{-1} and 1792 cm^{-1} respectively with the change from the liquid to the vapour phase. The ratio of the strengths of the bands 1752 cm^{-1} and 1792 cm^{-1} is, however, much smaller than that of the bands 1735 cm^{-1} and 1778 cm^{-1} due to the liquid. This was overlooked by Forbes and Myron (1961). Figure 2(b) shows that the strengths of the bands 1735 cm^{-1} and 1778 cm^{-1} due to both 3% and 1% solutions in benzene are in the ratio 1 : 3, there being no further reduction in the strength of the band 1735 cm^{-1} in this concentration range. Figure 2(c) shows that the ratio is larger in the case of the solution in chloroform than that for the solution in carbon tetrachloride, as observed by previous workers (Jones *et al*, 1959). The dotted curve in figure 2(c) for the 0.2% solution in carbon tetrachloride shows a reduction in the strength of the band 1735 cm^{-1} with the lowering of concentration of the latter solution to 0.2%.

These results thus show that the band or the Raman line at 1735 cm^{-1} persists under all conditions and even in the spectrum of the vapour, but there is some dependence of the influence of the solvent molecule on the concentration of the solution in particular ranges of the concentration. These results can not be explained on the hypothesis of the presence of associated molecules in the liquid. Also, Fermi-resonance can not explain the observed facts for the simple reason that the relative intensities of the two Raman lines can not change without change of frequencies of both of them (Placzek, 1934). It has been concluded by Forbes and Myron (1961) that the assignment of the line 1735 cm^{-1} to an overtone frequency is unsatisfactory but they have not proposed any satisfactory assignment of the line. It is possible however, to offer a new hypothesis which can explain the observed changes in the relative strengths of the two C = O bands of benzyl chloride and substituted benzoyl chlorides more satisfactorily.

Perhaps the clue to the explanation of the origin of the line 1735 cm^{-1} of the benzoyl chloride molecule is provided by the Raman spectra of cinnamyle chloride and phenyl acetylchloride. As shown in figure 3 both the molecules contain the phenyl group and also the C = O group, but while the former molecule gives respectively two Raman lines at 1727 cm^{-1} and 1746 cm^{-1} of equal intensities,

the latter molecule gives only one Raman line at 1797 cm^{-1} . Thus the second line of lower frequency due to $\text{C}=\text{O}$ stretching vibration occurs only when the

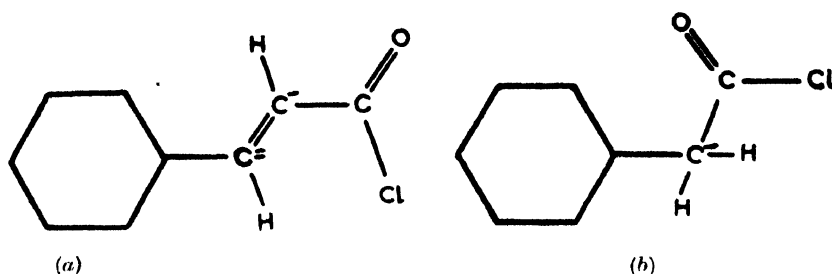


Figure 3. (a) Cinnamyle Chloride
(b) Phenyl acetyl Chloride

COCl group is connected to a carbon atom which again is connected to a third carbon atom through a $\text{C}=\text{C}$ bond. If the phenyl ring be in the plane of the paper in figure 3(a), the $\text{H}-\text{C}'-\text{C}$ group is also found to be in that plane, while the other two bonds of the C' -atom forming the double bond between C' and C'' atoms may be imagined to be in the vertical plane. Hence, as in the case of benzene, the $\text{C}'-\text{H}$ and $\text{C}'-\text{C}$ bending vibrations can be both in the plane of the paper and perpendicular to it, as in the case of $\text{C}-\text{H}$ vibration of the benzene molecule. In the case of phenyl acetyl chloride, however, the C' atom has all the four bonds arranged tetrahedrally so that the $\text{C}'-\text{C}$ bending vibration is only of one type. If it is assumed now that COCl group has freedom of rotation about the $\text{C}-\text{C}'$ single bond the $\text{C}=\text{O}$ group will in one configuration be perpendicular to the plane of the paper and in another configuration it will be in the plane of the paper. Considering all the molecules in the liquid, it may be assumed that half of them have the first configuration and the other half the second configuration. It is next assumed that during $\text{C}=\text{O}$ stretching vibration a little bending of the $\text{C}'-\text{C}$ and $\text{C}-\text{Cl}$ bonds takes place and that the contribution of such bending to the $\text{C}=\text{O}$ stretching frequency is larger in the case of the in-plane bending mentioned above than that of the out-of-plane bending. So, when the $\text{C}=\text{O}$ group is perpendicular to the plane of the paper the $\text{C}=\text{O}$ stretching frequency is smaller and the larger frequency is to be attributed to the configuration with the $\text{C}=\text{O}$ group in the plane of the paper. In the case of cinnamyle chloride there being equal probability of the two configurations in the liquid, the two Raman lines 1727 cm^{-1} and 1746 cm^{-1} are of the same intensity (Magat, 1936a). In the case of phenyl acetyl chloride, however, for all orientations of the COCl group about the $\text{C}'-\text{C}$ bond the $\text{C}'-\text{C}$ bending frequency is the same and consequently, the $\text{C}=\text{O}$ stretching frequency has a single value which is about 1797 cm^{-1} .

To justify the above hypothesis it has to be pointed out that in the case of the benzophenone molecule there is very little probability of free rotation of the OCC_6H_5 group about the $\text{C}-\text{C}$ bond between the carbon atom of the $\text{C}'=\text{O}$ group and that

of the other phenyl group and actually it gives only a single broad line at 1653 cm^{-1} although there is a line at 848 cm^{-1} . In the case of acetophenone also, the CH_3 group and the oxygen atom being seats of opposite charges the freedom of rotation of the OCCH_3 group about $\text{C}-\text{C}$ bond between this group and the phenyl group is restricted in the liquid. Actually, this molecule in the liquid state also gives a broad line at 1678 cm^{-1} the width being about 20 cm^{-1} . In this case also there is a line at 850 cm^{-1} . The width of the line due to $\text{C}-\text{O}$ vibration in these two cases may be due to slight deviations from the planar configuration caused by surrounding molecules. It is true that in the case of benzaldehyde the CHO group being much smaller, there may be free rotation of the group in the liquid, but in this case the hydrogen atom being much lighter, it appears to move with the carbon atom during $\text{C}=\text{O}$ stretching oscillation and only the contribution from the bending of the $\text{C}-\text{C}$ bond is to be considered. The difference between the frequencies of the $\text{C}=\text{O}$ vibration for the two orientations of the OCH group with respect to the plane of the phenyl group is expected to be about half of that observed in the case of cinnamyl chloride. Only a broad line is observed in this case, but its width being about 26 cm^{-1} (Magat, 1936b), it can be assumed to consist of two unresolved broad lines at a distance of about 13 cm^{-1} from each other.

If we consider now the case of the benzoyl chloride molecule it is found that molecule has certain special features as far as the above hypothesis is concerned. First, both the oxygen and chlorine atoms are seats of negative charges and taking the $\text{C}-\text{C}$ distance in acetaldehyde (Ackermann and Mayer, 1936) and the dimensions of the atoms given by Chandrasekharan *et al* (1968) and assuming the $\text{C}-\text{C}-\text{Cl}$ angle to be about 110° in the configuration and the OCCl group to lie in the plane of the phenyl group, the distance between the hydrogen atom in the ortho-position and the adjacent chlorine atom is found to be about 2.3 \AA . So, there is likelihood of formation of weak intramolecular $\text{H}\cdots\text{Cl}$ bond, but if there be external disturbing forces a free rotation of the OCCl group about the $\text{C}-\text{C}$ bond can take place. In the pure liquid the $\text{O}=\text{C}-\text{Cl}$ group of the neighbouring molecules provide such disturbing forces so that about 37% of the molecules have the non-planar configuration giving the line 1727 cm^{-1} . In the vapour state although the external forces disappear only about 30% of these non-planar molecules are converted into those of planar configuration probably because in the remaining molecules the OCCl group overcomes the potential barrier due to the energy acquired during free rotation. The enhancement of the two frequencies due to the vapour may be due to the removal of the influence of the permanent electric moment of the $\text{C}=\text{O}$ groups of the neighbouring molecules as pointed out in the case of ketones by Gray and Hidalgo (1952).

In the solution in chloroform the $\text{C}-\text{H}$ group of the solvent molecules seems to be responsible for the rotation of the OCCl group of a larger number of molecules because the $\text{H}\cdots\text{Cl}$ bond in the planar configuration is weakened by the presence

of the C—H group of the chloroform molecule in its neighbourhood, so that the phenyl group rotates about the C—C bond. Methylene chloride molecules also exert similar influence. As the chlorine atom of the C—Cl group of the chlorobenzene molecule is the seat of a small negative charge it does not rotate the OCCl group as strongly as the C—H group of the chloroform molecule. On the other hand the flat benzene ring of the chlorobenzene molecule offers more hindrance to the rotation of the phenyl group of the benzoyl chloride molecule about the C—C bond than that offered by the chloroform molecule owing to the tendency of the formation of feebly associated groups in the former solution as observed in the case of pure benzene (Sirkar *et al*, 1964). In the solution in benzene also similar influence of the benzene molecules increases the number of benzoyl chloride molecules having a planar configuration.

When the temperature of pure benzoyl chloride is raised to 95°C, the probability of the O = C—Cl group of a neighbouring molecule coming near the same group of a molecule diminishes and therefore the number of molecules of non-planar configuration diminishes. When the liquid is frozen and cooled to -180°C the lattice seems to consist of the molecules of both the configurations and the number of those having the planar configuration seems to increase on solidification.

In the case of benzoyl bromide the bromine atom is larger than the chlorine atom (Schoppe, 1936), so that the distance between the outer electrons of the bromine atom and the hydrogen atom is reduced by about 0.2Å. It seems that in this case the Br...H bond is stronger than the Cl...H bond formed in benzoyl chloride so that the influence of the O = C—Br group of the neighbouring molecules can not deflect the O—C—Br group of any molecule from the plane of the phenyl ring. Hence only one line due to such molecules is observed at 1769 cm⁻¹ (Magat, 1936a). The line, however has a breadth of about 25 cm⁻¹ probably due to slight deviations in some of the molecules from the planar configuration produced by thermal agitation. It would be interesting to study the structures of the single crystals of benzoyl chloride and benzoyl bromide to find out whether the two molecules have different structures as suggested above.

An attempt might now be made to explain the C = O frequencies observed in the spectra of at least a few substituted benzoyl chlorides. The results reported by Forbes and Myron (1961) show that parachloro-, parabromo- and paraiodobenzoyl chloride and also toluyl chloride give almost the same pair of lines at about 1782 cm⁻¹ and 1740 cm⁻¹ respectively with almost the same relative intensities as observed in the case of pure benzoyl chloride. The hypothesis given above can explain these observed facts satisfactorily, because the substitution in the para position of simple atoms like Cl, Br and I or the simple group like CH₃ does not hinder the rotation of the phenyl group about the diameter through the carbon atoms at positions 1 and 4. Substitution at the ortho-position makes the problem more complicated. In the case of the orthochlorobenzoyl chloride

molecule if the two chlorine atoms were near to each other in the plane of the phenyl group, the distance between their centres being almost about 2.3Å, they would strongly repel each other. So, in all probability only the oxygen atom comes near the chlorine atom attached to the phenyl group and the chlorine atom of the $O = C - Cl$ group goes near the hydrogen atom attached to the carbon atom at position 6 and forms a weak $H \cdots Cl$ bond there. The $C - C = O$ angle being about 124° in such compounds (Chandrasekharan *et al*, 1968), the distance between the oxygen atom and the chlorine atom attached to the phenyl ring becomes larger in this configuration of the molecule and therefore the repulsion between the two atoms becomes much weaker. In a solution in carbon tetrachloride the surrounding molecules of the solvent do not produce any force strong enough to deviate the $O = C - Cl$ group from the plane of the phenyl ring and therefore the line near 1790 cm^{-1} due to the $C = O$ vibration is expected to become much stronger and the other line near 1740 cm^{-1} to become much weaker. Such results have actually been reported by Forbes and Myron (1961).

The results observed for meta-substituted benzoyl chloride by Forbes and Myron (1961) are still more complicated. While meta fluorobenzoyl chloride dissolved in carbon tetrachloride gives two equally strong bands at 1782 and 1755 cm^{-1} respectively, the solutions of the metachloro-, metabromo- and metaiodo benzoyl chloride yield a very strong band at about 1765 cm^{-1} with a very weak band of wave number varying from about 1800 cm^{-1} to about 1812 cm^{-1} . On the hypothesis of freedom of relative rotation about the $C - C$ bond mentioned above it has to be concluded that the fluorine atom being the smallest of the above substituents, the fluorophenyl group can rotate freely about the $C - C$ bond while the heavier substituents hinder such rotation. The weak peak of higher frequency in the latter cases may be due coupling of slight stretching of the $C - X$ bond with the $C = O$ stretching vibration. In the case of meta methoxy benzoyl chloride on the other hand, the weak companion of the strong band at 1776 cm^{-1} has the lower wave number 1736 cm^{-1} . Thus in this case again the methoxy phenyl group is stationary in the solution in carbon tetrachloride while the $O - C - Cl$ group in a few of the molecules rotates about the $C - C$ bond as in the case of the unsubstituted molecule.

The Raman spectrum of benzoyl chloride in the solid state at -180°C shows five new low frequency lines given in table 2 in which such lines observed in the case of benzene have also been included. Microphotometric records of the lines are shown in figure 4. (Plate 8B).

If the line 95 cm^{-1} of benzene were assumed to consist of two unresolved lines it would appear from the results given in table 2 that both the crystals give the same number of low-frequency lines with similar relative intensities. So, as pointed out in the case of benzene (Sirkar *et al*, 1964) there may be two types of

molecules in the unit cell so that each of the angular oscillations of the phenyl group is split up into two components. It is difficult, however, to come to any definite conclusion regarding the structure of these two types of molecules from these results alone.

Table 2. $\Delta\nu$ in cm^{-1} Crystals at -180°C

C_6H_6 at -180°C Sirkar and Ray (1950)	$\text{C}_6\text{H}_5\text{COCl}$ at -180°C
47 (1)	35 (1)
53 (2)	50 (4)
74 (5)	56 (4)
95 (1b)	70 (5)
134 (3)	88 (1)
	104 (5)

Origin of two $\text{C}=\text{O}$ frequencies in lactones

It has to be pointed out that in the cases of some of the lactones studied by Jones *et al* (1959) the $\text{C}=\text{O}$ group is situated in the molecule in such a way that the carbon atom of the group forms a closed ring with other carbon atoms and an oxygen atom. In the case of β -cyclopentyl $\Delta^{\alpha\beta}$ butenolide, for instance, the ring consists of four carbon atoms and an oxygen atom as shown in figure 5(a). Ordinarily, the ring can have a planar structure with the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds in the vertical plane. It is interesting, however, that all the bonds of the carbon atom of the CH_2 group are single bonds and arranged tetrahedrally. The $\text{C}-\text{O}$ and $\text{O}-\text{C}$ bonds can therefore have two possible positions, one in the plane of the paper as in figure 5(a) and another inclined to it as shown in fig. 5(b). In the latter case the

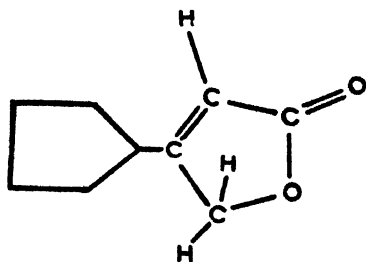


Fig. 5(a)

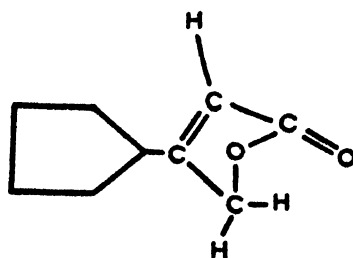


Fig. 5(b)

C = O group is also inclined to the plane of the paper. It can now be seen that while in figure 5(a) the C = O stretching vibration involves in-plane bending of the C—C and C—O bonds, in figure 5(b) such a vibration involves out-of-plane bending of both these bonds. Hence in this case the frequency of the C = O vibration in the former structure should be higher than that in the latter one. Actually, the solution of the molecule in carbon tetrachloride gives a strong band at 1785 cm^{-1} and a weak band at 1756 cm^{-1} . In the solution in chloroform, however, the first band becomes very weak while the band at 1750 cm^{-1} becomes very strong. It is to be concluded, therefore, that in the solution in carbon tetrachloride the ring formed by the four carbon atoms and the oxygen atom lies in the plane of the paper as in figure 5(a) and in the solution in chloroform the hydrogen atom attracts the oxygen atom of the ring and forces the ring to assume a bent structure as shown in figure 5(b). It is, evident however, that even in the former solution a few of the molecules have the ring with the bent structure giving the band 1756 cm^{-1} and in the latter solution also there are a few molecules with the ring of planar structure shown in figure 5(a). The influence of the C—H group of the chloroform atom mentioned above forces the ring to assume the bent structure shown in figure 5(b).

It is to be concluded from the above results that whenever there is any freedom of rotation about a particular bond in a molecule the structure of the molecule in state of aggregation may depend on environment. In the cases of the molecules discussed above the C = O stretching frequencies seem to furnish information about the relative populations of the molecules of different structures in the different environments.

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REFERENCES

- Ackermann, Ph. G., and Mayer, E., 1936, *J. Chem. Phys.*, **4**, 377.
 Chandrasekharan, R., Mallikarjunam, M., Chandrasekharan, G. and Zand, R., 1968, *Current Science*, **37**, 91.
 Forbes, W. B. and Myron, J. J. J., 1961, *Canad. J. Chem.*, **39**, 2452.
 Gray, E. and Hidalgo, A., 1952, *Compt. Rend.*, **235**, 152.
 Jones, R. N., Angell, C. L., Ito, T and Smith, R. J. D., 1959, *Canad. J. Chem.*, **37**, 2007.
 Magat, M., 1936, *Annual Tables of Numerical Constants*, **36**, p. 84.
 Placzek, G., 1934, *Handbuch der Radiologie*, **6**, Part 2, p. 325.
 Rao, C. N. R. and Venkataraghavan, R., 1962, *Spectrochim. Acta.*, **18**, 273.
 Schoppe, R., 1936, *Zeit Physik. Chem. B.*, **34**, 461.
 Sirkar, S. C., Mukherjee, D. K. and Bishui, P. K., 1964, *Indian J. Phys.*, **38**, 181.